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Conformational equilibria and the glass transition

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Abstract—Solutions of the conformationally inhomogeneous compounds 2-chlorobutane, chlorocyclohexane and *trans*-1,2-dichlorocyclohexane in glass-forming liquids (Nujol, butyl chloride and some phthalates) were investigated by i.r. absorption spectra. Freezing the conformational equilibrium at the glass transition of the solutions was observed. The method of using conformationally inhomogeneous compounds as a probe for the determination of the glass transition temperature (T_g) is proposed. The necessity of taking into account the glass transition process in interpreting results obtained for the temperature range $T < T_g$ has been shown. The possibilities of the application of the proposed method to polymers have been explored, and T_g of polystyrene has been determined.

INTRODUCTION

When studying the effect of the medium on the thermodynamic parameters of conformational equilibria, a great number of solvents, differing in their physicochemical properties have been used, liquids or solutions usually being investigated over a wide temperature range. Some solvents, used in such conformational analyses, do not crystallize but turn into a glassy state with decreasing temperature. Several liquids, which exist as a mixture of conformers, are also able to form glasses. In this connection there arises a question of interpreting experimental data obtained for temperatures lower than that of the glass transition of liquids or solutions. In the literature of conformational analysis, no proper answer can be found, because, in practice, the influence of the glass transition on conformational equilibria has not been studied. In this paper the influence of the glass transition on conformational mobility has been investigated by i.r. absorption spectroscopy.

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EXPERIMENTAL

The experimental technique was as follows. The conformationally inhomogeneous compound was dissolved in the glass-forming liquid. Then the temperature dependences of the integrated intensities of the i.r. absorption bands of the compound were measured.

The i.r. spectra were obtained with a UR 20 spectrometer and processed by computer. For investigating weak bands spectral accumulation was used. In cases of partial overlapping spectral contours, their distribution was deduced according to the method proposed in Ref. [1].

Temperature measurements were carried out with the help of a one-beam cryostat, cooled with liquid nitrogen. The average cooling rate was $0.01\,K \cdot s^{-1}$. Temperature was measured by a copper–constantan thermocouple. The error was less than ± 0.5 K.

RESULTS AND DISCUSSION

The conformationally inhomogeneous compounds investigated and some of their characteristics are listed in Table 1. The vibrational spectra and structures of **I–III** have been well studied [2–9]. Infrared absorption bands of the different conformers used in our study are included in the fourth column of Table 1. Compounds **IV** and **V** are less well known. It has been established [10] that the seven-membered ring of **IV** has a

Table 1. The conformationally inhomogeneous compounds and their characteristics

	Molecule	Conformations	Bands belonging to different conformers (cm^{-1})	$E^{\neq}$ ($kcal \cdot mol^{-1}$)	References
I	*Trans*-1,2-dichlorocyclohexane	*ee*	448, 514	13.5	[2–4]
		aa	461, 498		
II	Chlorocyclohexane	*e*	512	10.5	[2,5,6]
		a	560		
III	2-Chlorobutane	S_{HH}	464, 609	4.5	[7–9]
		S'_{HH}	525, 628		
		S_{CH}	671		
IV	8-Methyl-7,12-dioxaspiro[5,6]-benze[9,10]dodec-9-ene	*	628 637	≈ 10	[10]
V	2,4,4-Trimethyl-1,3-dioxa-5,6-benzocyclohexane	Twist Chair	600 590	≈ 6–9	[11]

*See text.